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Effect of Temperature and Elongation on the Liquid Diffusion and Permeation Characteristics of Natural Rubber, Nitrile Rubber, and Bromobutyl Rubber

D. DE KEE,[1] C. F. CHAN MAN FONG,[1] P. PINTAURO,[1] J. HINESTROZA,[1] G. YUAN,[1] A. BURCZYK[2]

[1] Department of Chemical Engineering, Tulane University, New Orleans, Louisiana 70118

[2] Defence Research Establishment Suffield, Box 4000, Medicine Hat, Alberta, T1A 9K6, Canada

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ABSTRACT: The diffusive properties of acetone, dichloromethane, and toluene in natural, nitrile, and bromobutyl rubber membranes at temperatures between 273 and 313 K and uniaxial elongations between 0 and 40% were investigated. As the temperature and elongation increase, the steady state flux increases, and the breakthrough time decreases. An increase in temperature leads to an increase in permeability, and small extensions do not cause significant changes in the diffusive properties. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78 1250–1255, 2000

Key words: diffusion; stress-enhanced diffusion; permeation; elongation; rubber

INTRODUCTION

Natural and synthetic rubbers are widely used as protective materials.[1] To assess this protection, it is important to have reliable data on their permeation properties under exposure to common laboratory and industrial solvents such as acetone, dichloromethane (DCM), and toluene.[2] In many applications, these materials are used as barriers over a range of temperatures and can be stretched to various degrees. It is, therefore, desirable to investigate the effects of temperature and elongation on their diffusive properties.

Several authors[3–6] have examined the diffusion of various solvents through different polymeric membranes. An increase in temperature leads to an enhancement of diffusion, and over a limited temperature range, the diffusive parameters follow an Arrhenius-type relation.[4–7] The effect of elongation depends on the nature and size of the penetrants, the barrier material, and, in addition, the magnitude and direction of the extension. Barrie and Platt[8] investigated the diffusion of hydrocarbons into rubber crosslinked with dicumyl peroxide and found that for an extension of up to 70%, no significant change in solubility and diffusivity was observed. At higher extensions, the permeability decreased with increasing extension. Several authors[5,9–11] have observed that if the extension is less than a critical value, the effect of the extension on permeability is negligible. A decrease in permeability followed by an increase as the extension increases has also been reported.[11–13] Wolf and Fu[5] observed an increase in diffusion when the applied stress was above a critical value. Xia and Wang[14] stretched the membrane in the directions perpendicular and parallel to the direction of diffusion and found that the effect of elongation was more pronounced for the parallel stretching.

No previous studies have been made to predict the effect of elongation on the permeability of an untested penetrant/barrier system. In this article, we present the results of permeation experiments

Correspondence to. D. De Kee

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on three solvents into natural, nitrile, and bromobutyl rubber membranes at four temperatures ranging from 273 to 308K and elongations ranging from 0 to 40%.

EXPERIMENTAL

Permeation tests were carried out on natural rubber (SMR-L), nitrile rubber (Krynac 40E65 at 39.8% ACN), and bromobutyl rubber (Polysar Bromobutyl X2), with membranes of an average thickness of 0.65 mm. The glass-transition temperatures and densities of the natural, nitrile, and bromobutyl rubbers were 211.5, 263, and 207.2 K and 1.14, 1.20, and 1.09 g/cm^3, respectively. Further information is given in Li et al.[15] The penetrants were acetone (ACP Chemicals, Inc., St. Leonard, Canada) and DCM and toluene (BDH, Inc., Toronto, Canada). The boiling points, molecular weights, and densities at 293 K for acetone, DCM, and toluene were 329.6, 312.9, and 383.8 K; 58.08, 84.93, and 92.14 g/mol; and 0.79, 1.32, and 0.87 g/cm^3, respectively.

A 51-mm-diameter two-chambered permeation cell (ASTM F739) was used to expose the test sample to the challenge chemical. The cell was purchased from A. A. Pesce Labs, Kennett Square, PA. The challenge chamber had a volume of approximately 0.045 L and was equipped with a stoppered nozzle for the addition of test liquids. The collection chamber had a volume of approximately 0.1 L and was equipped with inlet and outlet ports to pass the collection medium across the inner surface of the test sample. The system was operated in an open loop configuration connecting the outlet port of the cell to a gas chromatograph (Hewlett–Packard model 5790 A) through a Valco program valve. Nitrogen at a flow rate of 100 mL/min was used as the carrier gas.

The ASTM cell was placed in a temperature-controlled chamber in which the temperature could be controlled to within 0.5 K. The cell and the penetrant were placed in the chamber set at the desired temperature for at least 10 min before measurements were taken.

A homemade stainless steel drawing apparatus was combined with the permeation cell to allow for permeation tests under external stress. The membrane was stretched uniaxially until the desired extension was achieved, and the elongated sample was then clamped in the cell by the two hemispheres being firmly tightened.

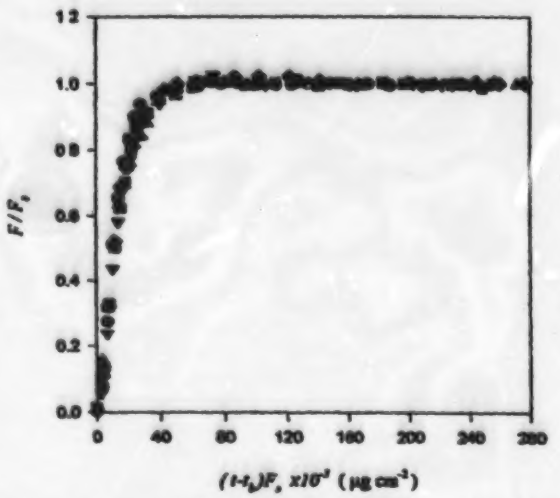

Figure 1 Plot of F/F_s versus $(t - t_b)F_s$ for acetone into nitrile rubber at 283 K for various elongations (%) ● = 0; ■ = 20; ▲ = 25; ▼ = 30; ◆ = 40.

Experimental details on the cell, drawing apparatus, and analytical technique are given in Li et al.[15]

RESULTS AND DISCUSSION

The experimental setup allowed us to determine the permeation flux, F, as a function of time and the breakthrough time, t_b. The F–t curves for a given solvent/rubber pair were similar for the entire range of elongations we considered. This suggests that it is possible to obtain a master curve through a plot of F/F_s versus $(t - t_b)F_s$, where F_s is the steady-state flux. This is confirmed in Figures 1–3, in which such plots are shown for the acetone/nitrile rubber system at 283 and 313 K and for the DCM/natural rubber system at 308 K. Similar plots were obtained for other solvent/rubber pairs.

From the F–t curves, it is possible to deduce the diffusion coefficients, D_0 and $D_{1/2}$, which are given by[6,7,16]

$$\ln(F\sqrt{t}) = \ln[2C_s\sqrt{(D_0/\pi)}] - \ell^2/(4D_0t) \quad (1)$$

$$D_{1/2} = 2\ell^2 \ln 2/(\pi^2 t_{1/2}) \quad (2)$$

where C_s is the saturation concentration, ℓ is the thickness of the membrane, and $t_{1/2}$ is the time at

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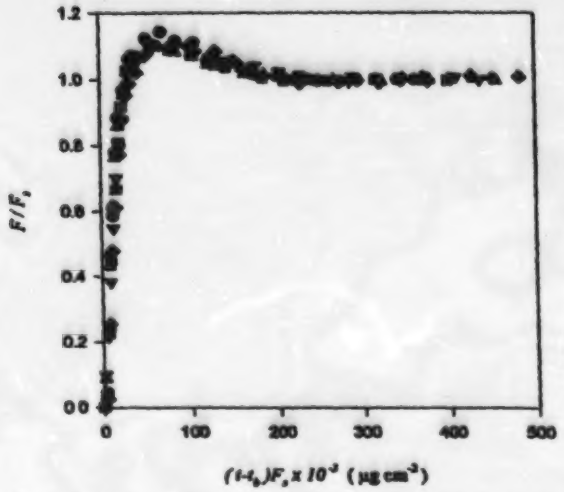

Figure 2 Plot of F/F_s versus $(t - t_b)F_s$ for acetone into nitrile rubber at 313 K for various elongations (%). ● = 0; ■ = 20; ▲ = 25; ▼ = 30; ♦ = 40

which $F = 0.5F_s$. Table I lists the values of D_0 and $D_{1/2}$ as well as F_s and t_b for several solvent/rubber pairs at various elongations and temperatures. Experiments were reproduced, and the variations observed were ±3 min for t_b, ±15% for F, and ±21% for D_0 and $D_{1/2}$. A comparison of Figures 1 and 2 suggests that there are two types of F–t curves. In type A (Fig. 1), F increases monotonically until the steady state is reached; thereafter, F remains constant. In type B (Fig. 2), F initially increases monotonically, reaches a maximum, and then decreases until the steady state is reached. Type-A behavior is observed in the permeation of acetone and DCM through natural rubber at all temperatures and at low temperatures (≤293 K) for all the other solvent/rubber pairs considered here. The results suggest that one of the effects of temperature is a possible change in the shapes of the F–t curves. The cause for the existence of a maximum in F is not clear. Thomas and Windle[17] observed for a PMMA–methanol system that the thickness of the membrane initially increased linearly with time until a maximum was reached and then decreased to a finite constant thickness. A similar maximum in the curves of F–t with a sorption experimental setup was also reported, and it was attributed to the effect of the initial swelling of the membrane,[18] so it seems plausible that there is a relationship between the maximum in flux and the maximum in the thickness of the membrane. However, it is difficult to measure the thickness of the membrane during the test. We may also associate a stress τ with the swelling, and this swelling stress is one of the factors that influence the transport process. By choosing a suitable constitutive equation relating τ to concentration, we can predict a flux that has a maximum.[19,20] For a better fit between experimental data and calculated values of F, it seems that an extended Jeffreys model[21] is more appropriate than a simple Jeffreys model. This is a topic currently under investigation in our research group.

From Table I, it can be seen that an increase in temperature leads to an increase in D_0, $D_{1/2}$, and F_s and a decrease in t_b. This result is in agreement with previous investigations.[4] In the range of temperatures considered in this study, these quantities follow an Arrhenius-type formula. Figures 4 and 5 show typical $\ln(F_s)$ versus $1/T$ and $\ln(t_b)$ versus $1/T$ curves.

Table I shows that D_0, $D_{1/2}$, and F_s are slowly increasing functions of the extension ϵ, and t_b is a decreasing function of ϵ. As mentioned earlier, a small extension does not generally lead to a significant change in the permeability behavior. The more substantial change in t_b might be attributed to the thinning of the membrane, as previously noted by Yang[22] on studies of dichloropentane through stretched butyl rubber.

The maximum 40% extension we imposed is not sufficient to cause a structural change in the

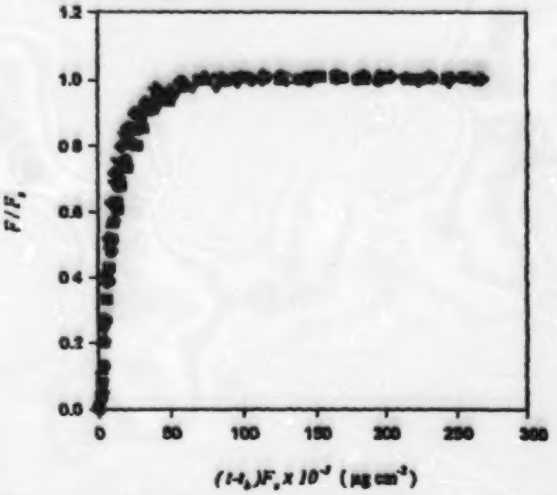

Figure 3 Plot of F/F_s versus $(t - t_b)F_s$ for DCM into natural rubber at 308 K for various elongations (%). ● = 0, ■ = 20; ▲ = 25; ▼ = 30; ♦ = 40.

Table I Values of D_0, $D_{1/2}$, F_s, and t_b for Several Rubber/Solvent Pairs at Various Elongations (ϵ) and at 273 K

Barrier	Temperature (K)	ϵ (%)	$D_0 \times 10^8$ (cm²/s)			$D_{1/2} \times 10^8$ (cm²/s)			$F_s \times 10^6$ (g/cm²/s)			t_b (min)		
			A	DCM	T	A	DCM	T	A	DCM	T	A	DCM	T
Natural rubber	273	0	1.4	6.4	2.2	3.6	60.3	36 3	0 10	26 87	1.9	228.9	13	25.6
		40	1.6	6.9	2.3	4.0	61.1	37.2	0.15	26.36	1.9	139.8	9.9	17.4
	293	0	7.5	13.7	8.2	17 4	90.8	70.4	0 86	45.37	6.1	34.7	7.9	11.4
		40	7.4	15.6	8.9	17.6	92.2	71.9	0.96	51.65	6 5	25 8	6.1	8.7
Nitrile rubber	273	0	2.1	4 3	0.2	28.5	80 1	10.0	9 5	30.8	1.5	24.9	8.5	84.4
		40	3.1	6.4	0.5	31.1	84.9	10.5	10.0	31.9	1.5	18.3	6.9	60 2
	293	0	7 4	10.2	1 2	52.3	102.5	21.9	14.2	62.5	4	13.2	5.8	36.7
		40	10.8	15.2	1.5	58.6	120 6	22.8	16.2	68.5	4.6	10.2	4.7	27.6
Bromobutyl rubber	273	0	N	2 0	0.6	N	30.5	18.6	N	7 3	2.0	N	38	51.3
		40	N	2.1	1.0	N	32.2	21.2	N	8.7	2.0	N	22.5	34.3
	293	0	N	5.1	1.9	N	54.5	37.3	N	16.3	6.0	N	16 5	23 0
		40	0.5	5.3	2 8	1 2	57.5	43.7	0.05	18.6	3 1	482	11.6	16.4

A = acetone, T = toluene, DCM = dichloromethane, N = no breakthrough after 24 h

membrane, and the linear theory of Larché and Cahn[23] is appropriate. They deduced that the chemical potential $\mu(\underline{\tau}, c)$ due to the presence of an applied stress $\underline{\tau}$ is given by

$$\mu(\underline{\tau}, c) = \mu(0, c) - \frac{1}{\rho}\left(\frac{d\mathbf{E}^s_{ij}}{dc}\tau_{ij} + \frac{d\mathbf{s}_{ijkl}}{dc}\tau_{ij}\tau_{kl}\right) \quad (3)$$

where ρ is the density, $\mathbf{E}^s_{ij}$ is the stress-free strain tensor that can be associated with the swelling mentioned earlier, and $\mathbf{s}_{ijkl}$ is the compliance tensor.

In our experimental setup, we extended the membrane uniaxially. We chose a rectangular Cartesian coordinate system (x_1, x_2, x_3) with the origin at the center of the membrane. The coordinates of a material point in the undeformed and deformed states are denoted by (X_1, X_2, X_3) and (x_1, x_2, x_3), respectively. If the membrane is extended uniaxially along x_1 by ϵ and the material is

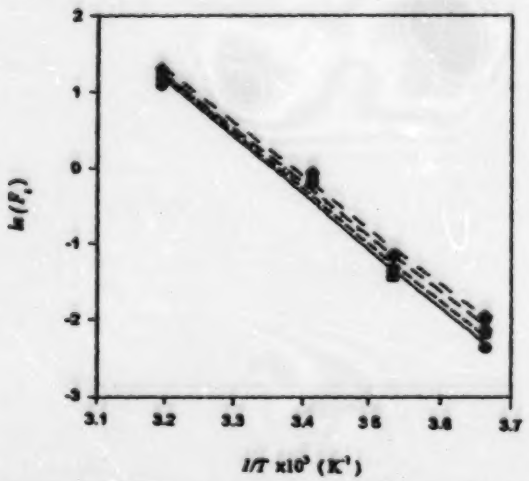

Figure 4 Effect of temperature on the steady-state flux, F_s, for acetone into natural rubber for various elongations (%). ● = 0; ■ = 20; ▲ = 25; ▼ = 30; ♦ = 40.

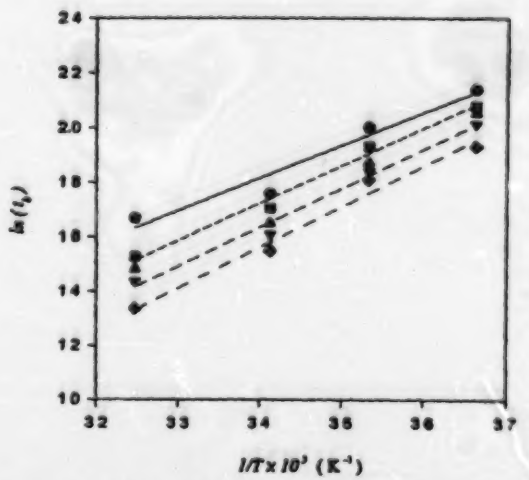

Figure 5 Effect of temperature on the breakthrough time, t_b, for DCM into nitrile rubber for various elongations (%). ● = 0; ■ = 20; ▲ = 25; ▼ = 30; ♦ = 40.

incompressible, the relationship between (X_1, X_2, X_3) and (x_1, x_2, x_3) is[24]

$$x_1 = \varepsilon X_1,\ x_2 = \varepsilon^{-1/2} X_2,\ x_3 = \varepsilon^{-1/2} X_3 \qquad (4)$$

The components of the strain tensor $\mathbf{E}_v$ are

$$E_{11} = (\varepsilon - 1),\ E_{22} = E_{33} = (\varepsilon^{-1/2} - 1) \qquad (5a\text{–}c)$$

The strain tensor $\mathbf{E}_v$ is now expressed as

$$\mathbf{E}_v = \mathbf{E}_v^c + \mathbf{E}_v^m \qquad (6)$$

where $\mathbf{E}_v^m$ contributes to the stress τ_v. The stress-free strain tensor is assumed to be isotropic and proportional to the concentration and can be written as

$$\mathbf{E}_v^c = \eta_1 c \delta_v \qquad (7)$$

where η_1 is a constant and δ_v is the Kronecker δ. We assume that the compliance tensor is independent of c. Substituting eq 7 into eq 3 yields

$$\mu(\underline{\tau}, c) = \mu(0, c) - \eta_1 \tau_u / \rho \qquad (8)$$

The constitutive equation of a linear elastic material is[24]

$$\tau_v = \lambda(\mathrm{tr}\ \underline{\underline{\mathbf{E}}}^m)\delta_v + 2\mu \mathbf{E}_v^m \qquad (9)$$

where λ and μ are Lamé's constants. Combining eqs 5(a–c), 6, 7, and 9 yields

$$\tau_u = 3\lambda(\varepsilon + 2\varepsilon^{-1/2} - 3 - 3\eta_1 c) + 2\mu(\varepsilon + 2\varepsilon^{-1/2} - 3 - 3\eta_1 c) \qquad (10)$$

Substituting τ_u into eq 8 and differentiating with respect to c result in

$$\frac{\partial \mu}{\partial c} = \frac{\partial \mu(0, c)}{\partial c} + \frac{3\eta_1(3\lambda + 2\mu)}{\rho} \qquad (11)$$

From eq 11, we deduce that the effect of elongation is an enhancement of diffusion, which is in agreement with our observation.

CONCLUSIONS

This work confirms our previous findings on the transport of organic solvents into geomembranes and rubbery membranes: an increase in temperature leads to an increase in permeability, and a small extension does not cause a significant change in the diffusive properties.

We believe further work needs to be done on stress-controlled diffusion so that the existence of a maximum in the F–t curves can be explained satisfactorily. The range of extension needs to be extended, and the possibility of structural changes should be examined. A nonlinear theory (covering larger extensions) that describes the effects of extension on diffusive properties is warranted.

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